A Study of the Raman Effect in Amorphous Solids.

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Abstract.

The paper describes the results of a study of the Raman effect in ten samples of optical glasses. The crown glasses show the phenomenon much feebler than the flints, a result analogous to that obtained in the experiments on classical scattering. Besides other weak bands, there are two prominent ones corresponding to about 500 and 1080 wave numbers which appear in practically all the samples. In those having lower refractive index, the former of these two is more intense. With increasing refraction, the latter gains in intensity over the former and becomes more prominent. The band at 1080 is represented by a prominent band extending from 8·5 to 10·7μ in the infra-red absorption.

1. *Introduction.*

In a recent paper[1] Prof. Raman has described the results of a study of the light scattering in a series of optical glasses. A peculiar effect, then known as weak fluorescence, was noticed by him in many of the samples examined. Subsequent investigations have shown that this phenomenon is a universal one and consists of certain modified radiations characteristic of the scattering substance. It is now well known that a study of these Raman radiations is extremely helpful in understanding various problems connected with molecular physics and a rapid progress has been made since the discovery with regard to gases, liquids and crystals.

[1] Jour. Opt. Soc. America, 15, 185 (1927).

Amorphous substances have however received comparatively little attention. Gross and Romanova [2] have studied one sample of crown glass and another of flint glass along with amorphous and crystalline quartz whereas Hollaender and Williams [3] have investigated a plate glass. The author has now undertaken a systematic investigation of a number of optical glasses differing from each other in composition and optical properties. The same group of glasses was used previously by Prof. Raman for studies in classical light scattering already referred to. The present paper consists of a description of the results obtained and a brief discussion of the same. An attempt is made to connect the results with (1) the variations in refractivity, chemical composition and the intensity of the classical scattering and (2) the nature of the amorphous state.

2. *Experimental arrangements.*

The samples examined were in the form of rectangular slabs $7 \times 7 \times 2$ cm. with one pair of end faces polished. The incident been which is obtained by condensing the light from a mercury arc lamp by means of a large glass condenser, was allowed to enter the glass slab through a side face. As this face is not polished, microscope cover slips were mounted on it by means of a thin layer of canada balsam in order to avoid the loss of light. A plane mirror was similarly stuck on the opposite face and served to reflect the light backwards. The scattered light emerges through a polished end face and is photographed by a quartz E_2 spectrograph supplied by Adam Hilger. As the scattering is very weak, even under such favourable conditions, an exposure of about 3 days had to be given in each case, in order to successfully photograph the modified radiations. All the glasses are of the same size and the period of exposure was about 3 days in all the cases, the other experimental arrangements remaining the same as nearly

[2] Z. f. Phys., 55, 744 (1929).
[3] Phys. Rev., 34, 380 (1929).

as possible. Thus a qualitative idea is also obtained as regards their relative scattering powers. In view of the long exposures and the extreme feebleness of the phenomenon, it is absolutely necessary that no direct light falls on the slit of the spectrograph lest it should result in an unfavourable back ground of continuous spectrum.

3. *Results.*

Table I contains the list of glasses examined, together with the physical properties, taken from the paper by Prof. Raman already referred to, that are necessary for the present paper. The results clearly indicate that crown glasses as a

TABLE I.

	Type.	Composition.	Refractive index.	Intensity of scattering relative to benzene = 1.
1	0·6781	Fluor crown	1·4933	0·18
2	U. V. 3199	U. V. crown	1·5035	0·12
3	0·3832	Prism crown	1·5163	0·14
4	0·3453	Silicate crown	1·5191	0·18
5	0·3439	Telescopic flint	1·5286	0·40
6	0·7550	Baryta light flint	1·5694	0·44
7	0·211	Densest borosilicate crown	1·5726	0·37
8	0·340	Ordinary light flint	1·5774	0·30
9	0·1266	Baryta light flint	1·6042	0·41
10	0·103	Ordinary flint	1·6202	0·42

rule show a much feebler scattering when compared to the flints. Table II contains the results obtained by the author. All the new radiations in the scattered light appear as more or less diffuse and broad bands extending over several Angstrom units and in many cases they are probably unresolved double or even multiple bands. That it is actually the case may be seen by comparing the results with those given in Table III. The numbers represent the frequency shifts of these bands

from the corresponding exciting lines. In all cases the centre of the band is measured. The numbers in the brackets represent the relative intensities of the corresponding bands. In Table III the results obtained by Gross and Romanova for crystalline and amorphous quartz and flint and crown glasses and by Williams and Hollaender for plate glass are given on the same wave number scale for comparison.

TABLE II.

	Composition	Raman frequencies						
1	Fluor Crown		460(0)					
2	U. V. Crown		480(1)		780(0)		1080(0)	
3	Prism Crown		460(0)					
4	Silicate Crown		460-520(2)		800(1)		1070(2)	1320(0)
5	Telescopic flint		460-520(3)		800(0)		1080(0)	
6	Baryta light flint		460(0)	640(1)	800(0)		1065(2)	1330(0)
7	Densest borosilicate crown	340(0)	460(0)	650(1)	800(0)		1090(2)	1320(0)
8	Ordinary light flint		460-500(2)		780(1)	1000(4)	1080(4)	1320(0)
9	Baryta light flint		460-500(2)			1000(4)	1080(4)	
10	Ordinary flint		460-520(2)			1000(4)	1080(4)	

TABLE III.

Crystalline quartz	125, 207, 264, 320, 358, 405, 463, 503, 526, 585, 633, 694, 746, 800, 943, 1020, 1075, 1163, 1220.
Amorphous quartz	213, 263, 323, 370, 440, 500, 625, 670, 740, 800-830, 1030-1090, 1190-1240.
Crown glass	208, 270, 330, 385, 450-510, 625, 670, 740, 800-830, 1030-1090, 1140-1190.
Flint glass	208, 260, 323, 370, 450, 510, 590, 670, 740, 800, 970, 1050, 1140, 1190.
Plate glass	268, 785, 1070, 1293, 1657, 1860, 2330.

4. *Discussion of the results.*

It is of great interest to note that the intensity relations are very much alike both for classical and Raman scattering. The Raman bands in crown glasses, especially the earlier members of the series, are very weak and can only be just detected whereas in the flints they are more easily observable. This result is completely analogous to that observed in classical scattering and suggests a close connection between the two phenomena. That such is the case is not altogether new as it is now well known that liquids like CS_2 and benzene which give rise to strong classical scattering also show intense Raman lines.

Unlike matter in the gaseous, liquid or crystalline state, these glasses show broad bands, a feature which appears to be very characteristic of amorphous substances. There is however little doubt that they are all due to molecular vibrations characteristic of the constituent materials. In this particular case however, silica is a primary constituent to which most of them seem to owe their origin as may be seen if we compare the results with those obtained by Gross and Romanova (*loc. cit.*) for fused silica which also shows broad bands unlike the sharp lines of quartz in the crystalline state. Such a result is probably due to the fact that the circumstances present in the amorphous solid are such that the vibrational energy is very imperfectly quantised.

The next question that naturally arises is whether there is any difference between the patterns obtained with different glasses. It may easily be seen from Table II that all the glasses show broad bands at about 500, 800, 1080 and 1330 wave numbers. The latter members of the series however show additional bands which may be due to the fact that the photographs are usually more intense in them. Of these bands the most prominent ones are at 500 and 1080 the

behaviour of which needs special mention here. Their relative intensities seem to show remarkable differences in various glasses. In the earlier members the one at 500 is distinctly more intense than the one at 1080 whereas in the latter ones the situation is just the reverse. In other words 1080 gains in intensity more rapidly than the one at 500 as we go up the series till it becomes quite prominent and sharp. In the last 3 flints it is very prominent and consists of two narrow bands which are well separated. Such variations may be significant if we remember that with increasing refraction the characteristic ultra-violet absorption frequencies are likely to come nearer and nearer the visible region. This in effect may be interpreted as a variation in the wave length of the exciting light with respect to a fixed absorption band. If the laws of variation of intensity for 1080 and 500 bands with varying exciting wave lengths are different, then the above phenomenon becomes explicable. [4]

It may be mentioned here that the prominent broad Raman band at about 1080 present in all these glasses is represented in infra-red absorption by one large complex absorption extending from 8·5 to 10·7μ, the maximum being at 9·7μ. [5]

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[4] S. C. Sirkar, Ind. Jour. Phys., 5,663 (1930)

[5] W. W. Coblentz, Investigations of Infra-red spectra, Carnegie Inst., (1906)